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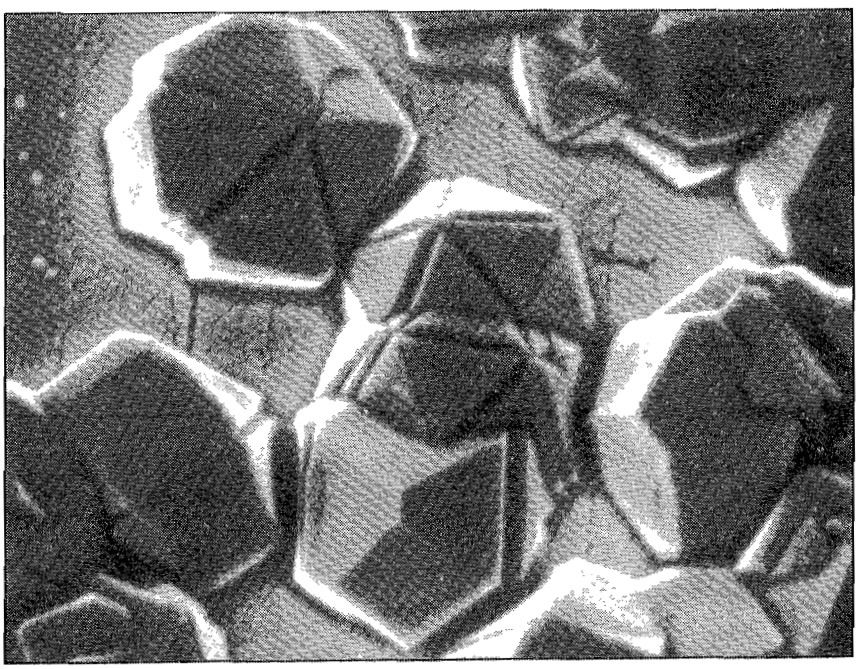
REPORT OF INVESTIGATIONS/1995

Adhesion of Diamond Films on Tungsten



UNITED STATES DEPARTMENT OF THE INTERIOR

UNITED STATES BUREAU OF MINES

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Cover: Diamond particles on tungsten showing multiple twinning (× 3,500).

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UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES
Rhea Lydia Graham, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric

cm	centimeter	nm	nanometer
h	hour	Pa	pascal
J/m^2	joule per square meter	pct	percent
mm	millimeter	V ac	volt, alternating current
μm	micrometer	°C	degree Celsius

U.S. Customary

Å	angstrom

Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

ADHESION OF DIAMOND FILMS ON TUNGSTEN

By K. J. Maggs,[1] J. W. Walkiewicz,[2] and A. E. Clark[3]

ABSTRACT

The U.S. Bureau of Mines has investigated the chemical vapor deposition of diamond films on tungsten substrates. The effects of deposition parameters on the adhesion of the films was determined. The films were produced using a hot filament chemical vapor deposition system. Parameters investigated were substrate temperature and methane concentration in the feed gas. Film quality, morphology, and composition were characterized by scanning electron microscopy and Raman spectroscopy. Adhesion testing was performed using an indentation technique, and the results were quantified by relating adhesion to interface fracture toughness. Diamond films with well-faceted crystalline morphology with grain size greater than 1 μm had poor adhesion properties regardless of substrate temperature or methane concentration. Diamond films with smooth morphologies consisting of rounded clusters of small (<0.2 μm) diamond crystallites and amorphous carbon phases displayed much higher adhesion, although the conditions that led to the growth of these films are not understood.

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[2]Supervisory metallurgist.
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INTRODUCTION

In the past decade, the production of diamond thin films by chemical vapor deposition (CVD) techniques has received considerable attention and has resulted in the commercial availability of several products that take advantage of the diamond's extreme hardness, high thermal conductivity, infrared transparency, and chemical inertness (*1-3*).[3] The use of diamond thin films as a wear-resistant coating for cutting tools has been impeded by the lack of adhesion displayed by these films on most substrates of interest, particularly cemented carbides (*4*). The adhesion of diamond films to these materials is adversely affected by cobalt used as a binder. Sintered, binderless tungsten carbide tools and techniques to etch away surface cobalt have been developed to improve the film-substrate adhesion properties (*5-6*). However, adhesion has not been improved to the point where reliable diamond-coated carbide tool bits are commercially available. Therefore, it is of interest to study the factors that affect adhesion of diamond films to carbides. Pure tungsten is useful as a substrate to effect these studies since, prior to diamond formation on the surface of a carbide-forming element such as tungsten, a carbide transition layer is formed upon which the diamond crystallites nucleate (*7-8*). The purpose of this U.S. Bureau of Mines (USBM) study was to determine the effects of methane concentration and substrate temperature on the adhesion of diamond films to tungsten. This work supports the USBM goal of providing inovative technologies to conserve domestic mineral resources.

No standard method of measuring the adhesion of diamond thin films has been established. Various papers have reviewed the techniques commonly used, including scratch, pull, and bend tests (*9-11*). Most of these methods have suffered from the lack of repeatable or quantifiable results that can be used to compare the adhesion of one film-substrate system to another. This work utilizes a brale indentation method and a quantification technique based on fracture mechanics to relate adhesion strength to interface fracture toughness.[4] The method was found to be a simple and efficient technique that can be used to compare results of adhesion testing of samples with varying film thicknesses and substrate materials.

EQUIPMENT AND PROCEDURE

DEPOSITION APPARATUS

Diamond film samples were prepared by hot filament chemical vapor deposition. The deposition reactor was a six-way stainless steel cross with 20-cm-diam arms, evacuated with an Alcetel vacuum pump. Methane and hydrogen feed gases were metered into the system, and operating pressures were maintained using MKS gas flow control equipment. Substrates were placed on a graphite substrate holder and heated with a boron nitride-graphite resistance heating element. Hot filament activation of feed gases was achieved using a parallel array of six straight rhenium filaments. Filament temperature was monitored with an optical pyrometer. Energy was supplied to the substrate heater and to the filaments with 110 V ac variacs. Substrate temperature was measured with a molybdenum sheathed Pt-Pt/Rh (type R) thermocouple in contact with the back of the substrate and controlled with an Omega PID controller.

SUBSTRATE PREPARATION AND CONDUCT OF TESTS

Substrates were prepared by cutting 4.8-mm slices from a 2.54-cm round of tungsten with an abrasive cutoff wheel. The substrates were ground through 600 grit, and the surfaces were scratched with 1-μm diamond paste to promote nucleation. At the end of this preparation, the surfaces were well covered with visible scratches from the diamond paste. The prepared substrates were cleaned with ethanol and blown dry. Samples were placed on the substrate holder, and the distance from filament to substrate was set at 7 mm. The reactor was sealed and a vacuum drawn to 0.133 Pa of pressure. At this point, feed gases were introduced, and an operating pressure of 13.3 kPa was maintained. The substrate heater and filaments were energized, and deposition was continued for approximately 48 h. Upon completion of the run, the substrate heater and filaments were turned off, and the substrate was allowed to cool to room temperature. Tests were conducted at substrate temperatures of 750, 850, and 950 °C, with methane concentrations of 0.3, 0.5, 0.75, and 1.0 pct, remainder hydrogen. Filament temperature was maintained at 2,100 °C for all tests.

ADHESION MEASUREMENT

Adhesion results were obtained using an indentation method. A Rockwell hardness tester with a brale type of diamond stylus was used to indent the film-substrate

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

[4]Personal communication from M. D. Drory and M. G. Peters, Crystallume, Inc., Menlo Park, CA, May 1990.

sample. The indentation produces an approximately circular area of interfacial delamination around the indentation site as a result of substrate deformation and uplift. According to a model developed by Drory and Peters,[5] a value for adhesion of the film to the substrate in the form of a normalized interface strain energy release rate, or interface toughness, was obtained using the equation:

$$G/Eh = (1/32)(\Delta/h)^2(a/h)^{-4}, \quad (1)$$

where G = interface fracture toughness, J/m^2,

E = Young's modulus of the film, 1.05×10^{12} Pa,

h = film thickness, μm,

Δ = height of substrate uplift, μm,

and a = crack length, mm.

The technique is an approximation that assumes mode I fracture at the interface of the film and substrate resulting from the plastic deformation of the substrate, and a circular delamination area. Mode II fracture mechanisms may also play a part in the failure of the film, and it was found that the indentation often produced a nonuniform deformation ridge resulting in some noncircular delaminations. After the samples were indented, the delamination site was photographed using an optical microscope with incident light illumination. Delamination areas were determined from these photographs using an image analyzer. After measurement, the delaminated portion of the film from each sample was removed with transparent tape and the cross section was imaged and photographed with the scanning electron microscope (SEM). Film thickness was determined from analysis of the photomicrographs. Surface profilimetry was conducted at Albany Research Center, USBM to measure the uplift produced by plastic deformation of the substrate during indentation and to confirm film thickness measurements.

FILM CHARACTERIZATION

Film morphology, quality, and graphitic content were characterized at the Idaho National Engineering Laboratory (INEL) by Raman spectroscopy, and by SEM at both Reno Research Center, USBM and INEL. Raman spectroscopy was performed with an AR^+ ion laser at wavelength of 514.5 nm. Laser spot size was approximately 1 μm in diameter. SEM characterization was used to determine crystalline morphology.

RESULTS AND DISCUSSION

ADHESION TEST RESULTS

Adhesion test data, compiled for the 12 original test samples, are shown in table 1. Interface fracture toughness versus methane concentration at the three substrate temperatures is shown in figure 1. Two samples, produced at 850 °C with 1.0 pct CH_4 and at 950 °C with 0.75 pct CH_4, have toughness values considerably higher than the rest. Excluding these two samples, interface fracture toughness did not vary significantly with methane concentration or deposition temperature. Visual examination of all samples produced showed the 2 samples with the highest toughness values differed in appearance from the other 10 samples. The majority of samples exhibited a gray, opaque appearance, while the two samples appeared clear. Closer examination of a fully delaminated portion of the clear film revealed a grayish-brown tint. Thickness of the clear films was within the range of thicknesses of the gray films. An attempt to repeat the results obtained at these two sets of deposition parameters was not successful, and resulted in two gray films with poor adhesion properties. The 850 °C, 1.0 pct CH_4 repeat sample suffered circular delaminations upon indentation that were comparable in size to those produced on the poorly adherent films. The 950 °C, 0.75 pct CH_4 repeat sample delaminated over 90 pct of the entire substrate surface as a result of one indentation. The lack of repeatability indicates that a parameter other than substrate temperature or feed gas composition controls the film quality and adhesive properties of the two clear films.

FILM CHARACTERIZATION

Scanning electron photomicrographs of a representative sample of a gray diamond film, sample 1 (0.3 pct CH_4, 750 °C), are shown in figure 2, and photomicrographs of one of the clear films, sample 8 (1.0 pct CH_4, 850 °C), are shown in figure 3. The photomicrographs show that the two types of films differ greatly in morphology. The gray film consists of well-faceted, highly twinned cubo-octahedral particles with a crystallite size of approximately 1 to 5 μm. The clear film shows a much smoother surface with no visible faceting. The crystallite size is approximately 0.2 μm or less, and surface features, which were observed, appeared to be rounded clusters of these small particles.

[5]Cited in footnote 4.

Table 1.—Adhesion test data

Substrate temp and sample	Methane concentration, pct	Film thickness (h), μm	Substrate uplift (Δ), μm	Crack length (a), mm	Interface fracture toughness (G), J/m^2
750 °C:					
1	0.3	4.52	6.45	0.49	0.0024
2	0.5	7.10	6.69	0.58	0.0048
3	0.75	8.70	4.86	0.43	0.0156
4	1.0	7.10	5.31	0.37	0.0182
850 °C:					
5	0.3	7.74	6.32	0.48	0.0123
6	0.5	8.70	6.26	0.46	0.0207
7	0.75	9.73	5.02	0.54	0.0132
8	1.0	9.43	5.96	0.32	0.0952
950 °C:					
9	0.3	6.90	6.18	0.31	0.0203
10	0.5	4.60	6.15	0.36	0.0073
11	0.75	5.01	4.75	0.14	0.2182
12	1.0	8.0	4.0	1.24	1.13×10^{-8}

Raman spectrographs for representative samples of the clear and gray films are shown in figure 4. Figure 4*A*, which is the spectrum of a gray film, shows a strong diamond peak centered at 1,332 wavenumbers. The spectrum in figure 4*B* was taken from a clear film and shows a diamond peak at 1,332 wavenumbers, a peak just off the diamond peak at about 1,355 wavenumbers, and a large extended peak centered in the 1,470 to 1,530 wavenumber area. The nondiamond peaks represent amorphous (diamond-like) carbon phases (12).[6]

DISCUSSION

The results presented above indicate that film morphology and composition play a much greater role in adhesion of diamond films to tungsten than the parameters of substrate temperature or methane concentration. When results from the two anomalous films are not considered, adhesion did not vary significantly over the experimental range. All of the gray films were similar in that the morphology consisted of relatively large (1 to 5 μm) well-faceted crystals of a type most commonly associated with CVD diamond films. The two clear films initially produced at 850 °C with 1.0 pct CH_4 and at 950 °C with 0.75 pct CH_4 were not of this morphology. SEM examination showed an extremely fine-grained texture with grain sizes of 200 nm or less. The Raman spectra contain features that have been ascribed to "composite" films with diamond and diamond-like, amorphous phases. The diamond-like phase is described as small (15 to 20 Å or less) regions of sp^2 bonding terminated with sp^3 bonds (*12*). High adhesion values reported for the clear films may be attributed to several factors. Small grain size would assist in the mechanical locking of the film to surface features on the substrate. The small grain size implies an increased nucleation density that would result in fewer interstitial voids and maximize surface area contact with the substrate. Increased ratio of grain boundary to bulk grain may result in pi-bond electrons associated with sp^2 structures being available for bonding to carbide structures on the substrate. Unfortunately, the factors that led to the production of the clear films have not been fully determined. Attempts to reproduce clear films resulted in gray films whose morphology and adhesive properties were similar to the majority of films produced.

SUMMARY

The effect of deposition parameters of substrate temperature and methane content on the adhesion of diamond films on tungsten substrates has been studied. Gray diamond films with grains larger than 1 μm and a Raman spectrum consisting of essentially pure diamond were found to exhibit poor adhesion. Adhesion properties of these films were not significantly affected by the variation of substrate temperature or methane concentration. Two clear films, which exhibited a Raman spectrum consistent with a composite of diamond and diamond-like carbon, were found to have significantly improved adhesion

[6]Personal communication from J. C. Ingram, ID Nat. Eng. Lab., Idaho Falls, ID, June 10, 1993.

properties. These films could be expected to have hardness and wear properties very similar to diamond films with Raman spectra indicative of essentially pure diamond and would, therefore, be useful in cutting applications.

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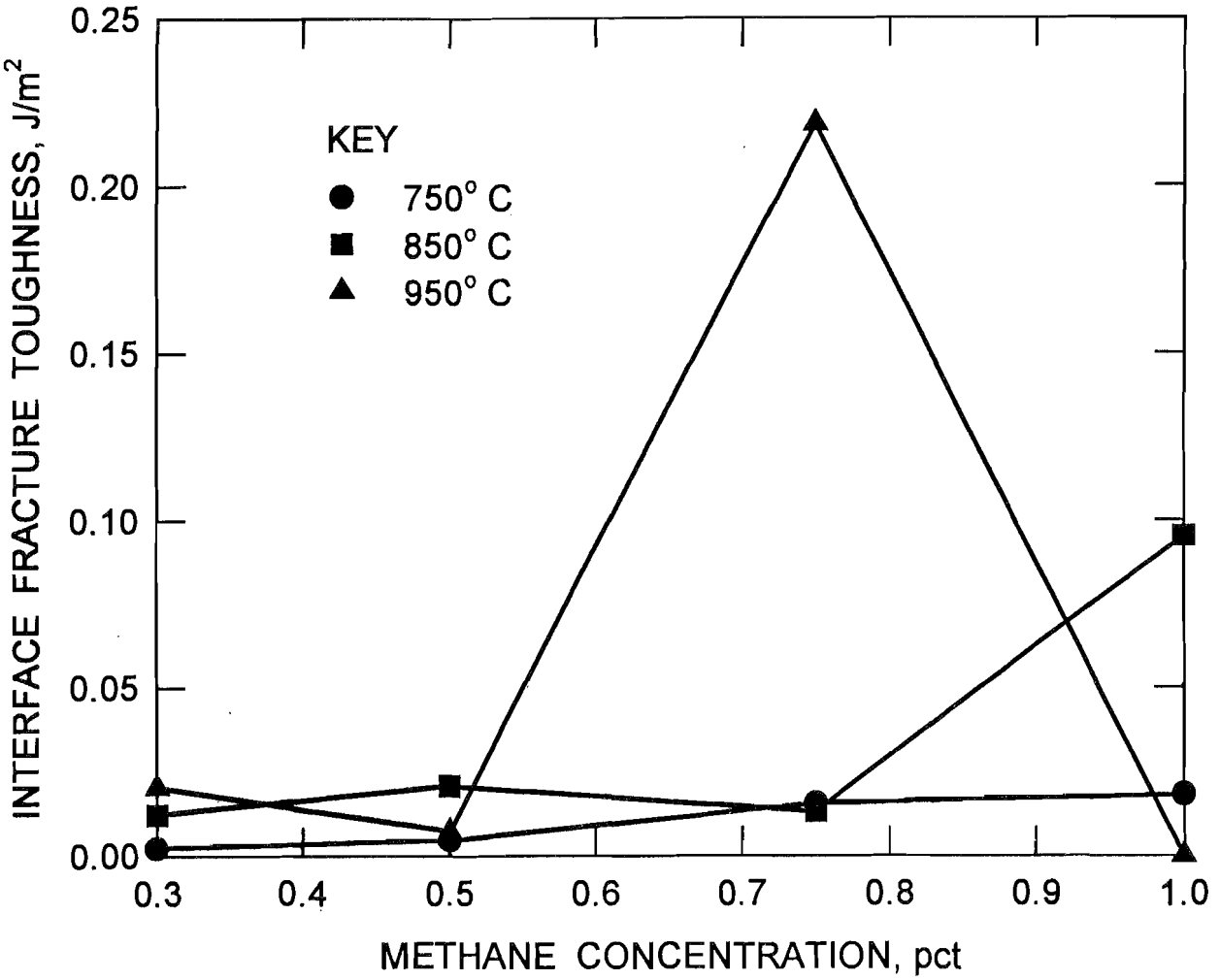
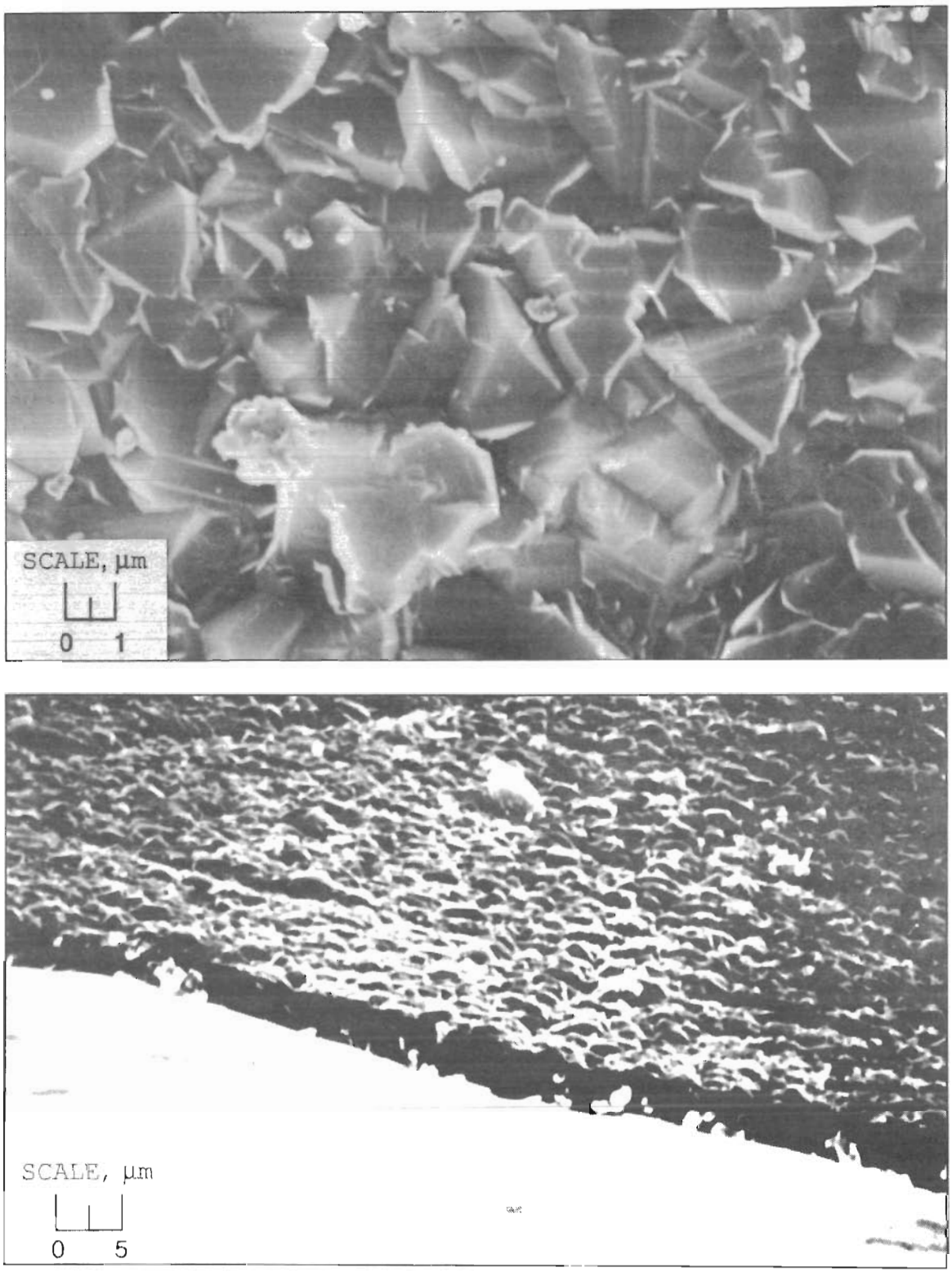
Figure 1



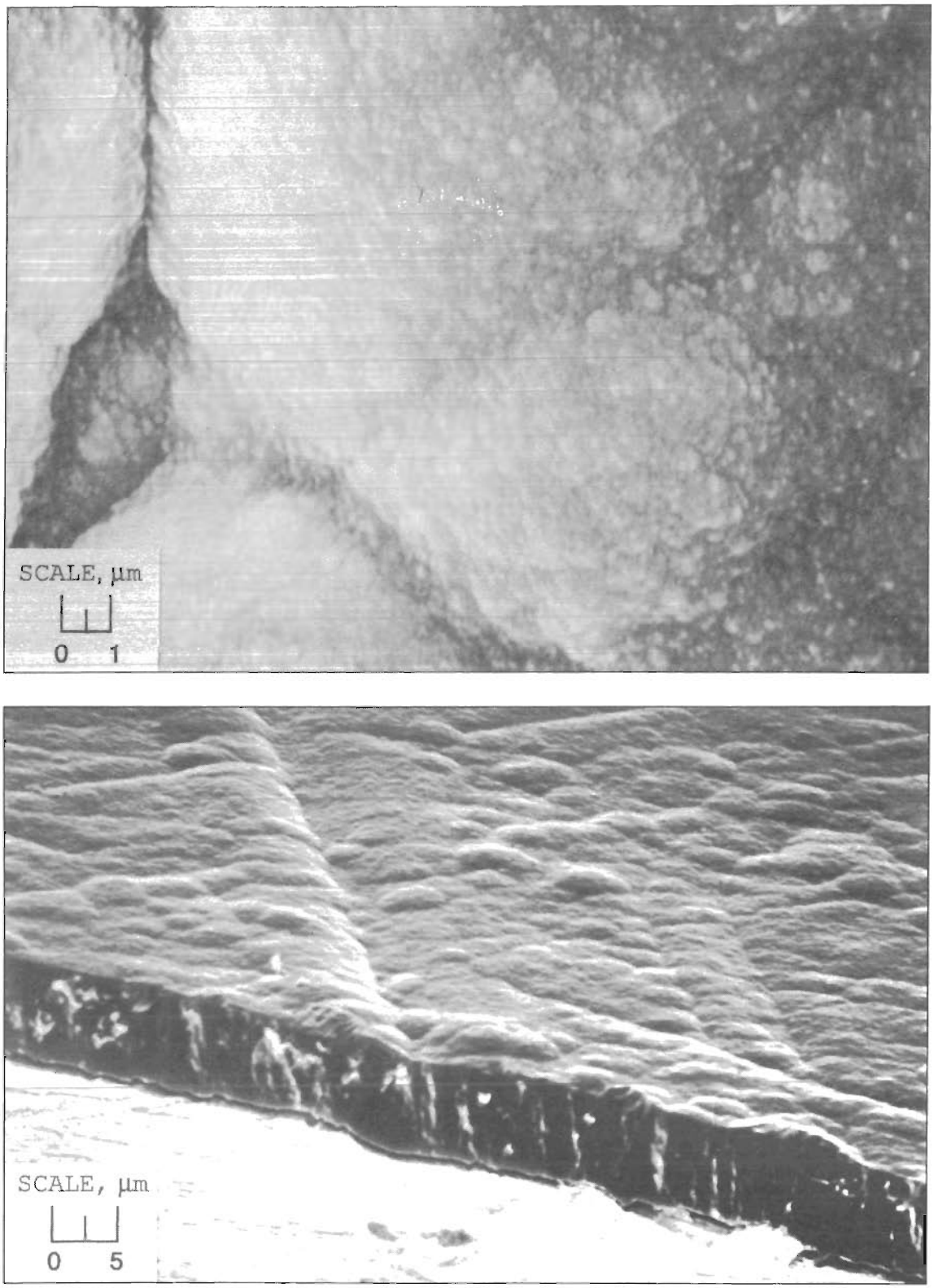
Interface fracture toughness versus methane concentration.

Figure 2



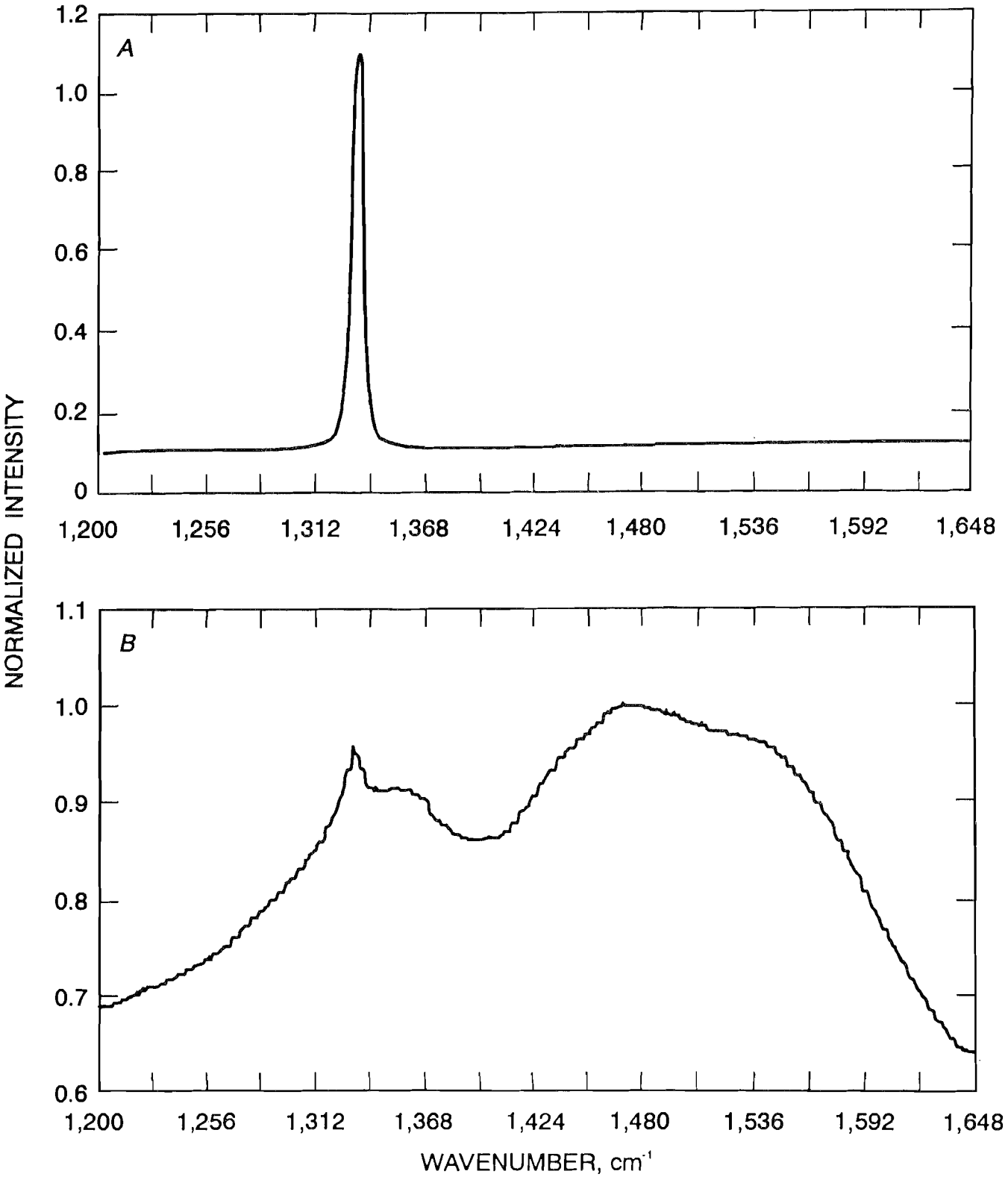
SEM photomicrograph of representative gray film, sample 1. Top, × 5,000; bottom, cross section (× 1,000).

Figure 3



SEM photomicrograph of representative clear film, sample &. Top, × 5,000; bottom, cross section (× 1,000).

Figure 4



Raman spectra. A, representative gray film, sample 1; B, representative clear film, sample 8.

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